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Supplementary Information

Alkaline earth ion exchange study in pure silica LTA zeolites using periodic first-principles calculations

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Table S1. Calculated standard chemical potential, in eV, of Na^+ and alkali earth ions in vacuum (vac) and in water (aq)

Ion (A)	$\mu^0_{A(vac)}$		$\mu^0_{A(aq)}$	
	PBE	DFT-D3	PBE	DFT-D3
Na^+	5.1573	5.1573	-2.3806	-2.4920
Ca^{2+}	18.1425	18.1425	-5.4051	-5.4369
Sr^{2+}	16.8687	16.8687	-5.4808	-5.5223
Ba^{2+}	15.2986	15.2986	-5.4066	-5.4183

The activity coefficient, γ_i, are calculated using Debye-Hückel equation:

$$\log(\gamma_i) = -\frac{A z_i^2 \sqrt{I}}{1 + B d \sqrt{I}}; \quad I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2$$

where z_i is the charge of the ion, d is the ionic diameter, in nm, I is the ionic strength, c_i is the concentration of the ion, n is total number of ion types and the sum in I is over each ionic type, i. A and B are constants calculated by fitting the experimental activity data to Debye-Hückel equation.

Table S2. Constants for activity coefficients of Na^+ and alkali earth ions, fitted on Debye-Hückel equation.

Ion	A	B (in nm^{-1})
Na^+	1.2055 ± 0.0095	9.6338 ± 0.2340
Ca^{2+}	4.7050 ± 0.0224	8.9327 ± 0.1407
Sr^{2+}	4.6856 ± 0.0191	6.3263 ± 0.0981
Ba^{2+}	4.6856 ± 0.0191	5.6045 ± 0.0869

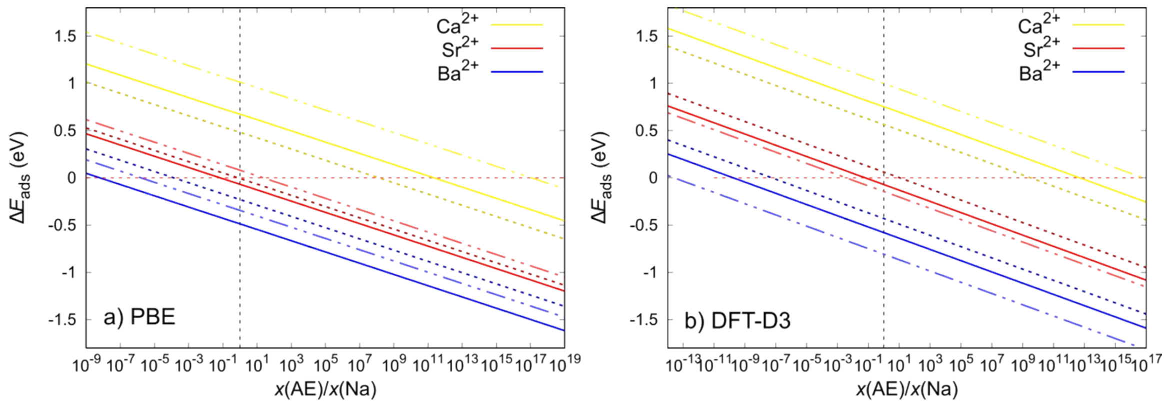

Figure S1. Adsorption energy difference, ΔE_{ads}, on site 1 (solid line), 2 (dashed-dotted line) and 3 (dashed line) as a function of the mole fraction ratio, x_{AE}/x_{Na}, between AE = Ca^{2+}, Sr^{2+} and Ba^{2+} ions and Na^+ ion, calculated using (a) PBE, and (b) DFT-D3. The Ca^{2+}/Na^+, Sr^{2+}/Na^+, and Ba^{2+}/Na^+ ΔE_{ads} are shown in yellow, red and blue, respectively.

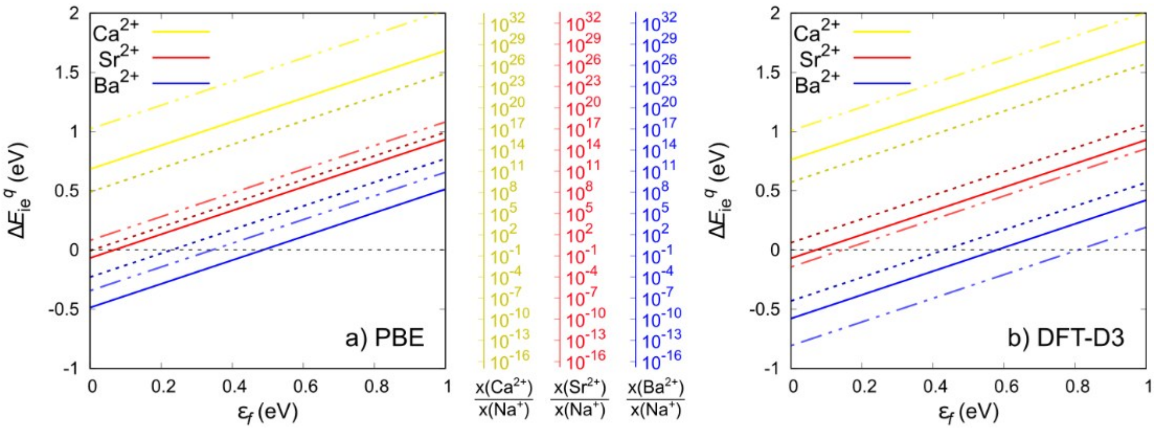

Figure S2. Ion exchange energy, ΔE_{ie}^{q}, as a function of the electron chemical potential, ε_f, for ions on site 1 (solid line), 2 (dashed-dotted line) and 3 (dashed line), calculated using (a) PBE, and (b) DFT-D3. The Ca^{2+}, Sr^{2+}, and Ba^{2+} ΔE_{ie}^{q} are shown in yellow, red and blue, respectively. The scales in the middle show the x(AE)/x(Na) ratio at which the $\Delta E_{ads}^{q} = 0$ eV.

Table S3. Ion exchange energies (ΔE_{ie}^{0}), in eV, of Na^+ with alkali earth ions on the three adsorption sites, calculated using PBE and DFT-D3.

Ion	PBE			DFT-D3		
	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
Ca^{2+}	0.6827	1.0880	0.4903	0.7623	0.9406	0.5729
Sr^{2+}	-0.0676	0.1476	-0.0063	-0.0703	-0.2100	0.0619
Ba^{2+}	-0.4865	-0.2773	-0.2290	-0.5788	-0.8740	-0.4303